New approaches to prepare nitrogen-doped TiO$_2$ photocatalysts and study on their photocatalytic activities in visible light

Mingyang Xing, Jinlong Zhang *, Feng Chen

Lab for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China

ARTICLE INFO

ABSTRACT

Nitrogen-doped TiO$_2$ nanocatalysts were successfully synthesized by adjusting a pH range using the ammonium nitrate and ammonia water as the nitrogen source. The samples were characterized by XRD, XPS and UV-DRS. When the total amount of ammonium nitrate and ammonia water was unchanged, different pH values were modified by changing the NH$_4$NO$_3$/NH$_3$·H$_2$O ratio to prepare nitrogen-doped TiO$_2$. The prepared photocatalyst showed the highest photo-activity for the degradation of 2,4-dichlorophenol (2,4-DCP) under visible light when prepared at pH 5.87. XPS analysis showed the presence of nitrogen in two states doped in TiO$_2$. The results indicated the photocatalytic activity of N-TiO$_2$ is varied with the change of pH values, the amount of the nitrogen sources and water. The experimental results showed that the higher activity is due to the variation in the concentration and states of nitrogen-doped in TiO$_2$. In the preparation methods, the photocatalyst was treated with the hydrogen peroxide before calcination, resulting in the decrease of nitrogen doped into the lattice and the photo-degradation rate of 2,4-DCP. The results suggested that the nitrogen source could be doped into the crystal lattice only in the form of reduction state as NH$_4^+$ ion during the calcination process.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Titanium dioxide has been extensively studied through the world and considered as reference photocatalyst in the degradation of organic pollutants, sewage treatment, air purification, disinfection due to its superior photocatalytic performance, non-selective degradation of various organics, deep mineralization rate, low cost, inert and non-toxic properties [1–3]. However, the wide band gap of TiO$_2$ (anatase of 3.2 eV, rutile of 3.0 eV) limits the absorption wavelength less than 387 nm, which is only 3–5% of the sunlight energy and holds back the practical applications. In addition, the high rate of electron–hole recombination on the surface and in the bulk phase of the catalysts, and the low photoelectric conversion efficiency hampers the practical applications of TiO$_2$ as photocatalytic materials. Many researchers have done a lot of work to modify the photocatalyst [4–6]. Asahi et al. found that nitrogen doping could reduce the band gap of TiO$_2$ and improve its photocatalytic activity in the visible-light region [7]. Then some reports of other non-metallic elements such as fluorine, carbon, boron and sulfur doped TiO$_2$ with photocatalytic activity under the visible light have appeared subsequently [8–11]. The

investigation of the photocatalytic activity of TiO$_2$ under visible light even indoor light has attracted great attention today.

Many kinds of nitrogen sources can be used in the preparation of N-TiO$_2$ which include organic nitrogen sources such as urea, sulfur urine and tri-ethylamine [12,13], and inorganic nitrogen sources such as ammonia, ammonium chloride and ammonium nitrate [14,15]. The influence of the pH values may be different when different kinds of nitrogen sources are used. As the pH value changed, many other factors could also be changed simultaneously such as the amount of nitrogen source. So it is difficult to actually investigate the effect of the pH value on photocatalytic activity of N-TiO$_2$ when the inorganic nitrogen sources are used. However, the systemic exploration of the concrete effect of pH value on the photocatalytic activity is very important to optimize the catalyst.

In this paper, nitrogen-doped TiO$_2$ was prepared by using ammonia water and ammonium nitrate mixture as nitrogen sources for the first time. The pH values could be changed by fixing the total amount of nitrogen sources NH$_4$NO$_3$/NH$_3$·H$_2$O ratio during the preparation. In this method, we investigated the effect of pH values on photocatalytic activity of N-TiO$_2$ while kept other parameters unchanged such as the amount of nitrogen source and water. The results indicated that the states of nitrogen doped could play an important role in the photocatalytic performance of N-TiO$_2$. At the same time, H$_2$O$_2$ was used in the preparation process of N-TiO$_2$ to investigate the nitrogen source doping in TiO$_2$ during the calcination.

* Corresponding author. Tel.: +86 21 64252062; fax: +86 21 64252062.
E-mail address: jlzhang@ecust.edu.cn (J. Zhang).

2. Experimental

2.1. Preparation of photocatalysts

10 mL tetrabutyl titanate (TBOT) was added drop wise to 40 mL deionized water, while stirring the solution for 5 h. After aged for 24 h at room temperature, the solution was filtered and washed with deionized water. To obtain TiO_2, the powders were dried in oven for 3 h and calcined at 400 °C for 4 h.

2.2. Preparation of N-TiO_2 in different conditions

The mixture of ammonium nitrate and ammonia water was dissolved in 40 mL deionized water while kept the total amount of ammonium unchanged. 10 mL TBOT was added drop by drop to the solution, while stirring the solution for 5 h. The solutions of different pH values of 5.14, 5.87, 7.36, 8.38 and 9.01 were prepared by changing the ratio of ammonium nitrate to ammonia water, and then aged for 24 h at room temperature. After filtration, the precipitate was washed with deionized water. The powders were dried in oven for 3 h, and then calcined at 400 °C for 4 h.

Using the same experimental method, we can modify different N/Ti molar ratios (0.5, 1.0, 2.0, 4.0) by changing the total amount of the nitrogen sources, while kept the molar ratio of ammonium nitrate to ammonia water at 3.4, and also can modify different H_2O/ Ti molar ratios (19, 38, 76, 152) by changing the amount of deionized water.

2.3. N-TiO_2 treated with H_2O_2 before calcination

3.6 g ammonium nitrate was dissolved in deionized water. 0.9 mL ammonia water was added to above ammonium nitrate solution and then 10 mL TBOT was added drop by drop to the solution, while stirring the solution at room temperature for 5 h. Nitric acid was added slowly until pH of the solution was 6.0. The solution was aged for 24 h at room temperature. After that, 40 mL H_2O_2 (7.5 wt.%) was added under vigorous stirring for 3 h. After filtration, the precipitate was washed with deionized water. The powders were dried in oven for 3 h and calcined at 400 °C for 4 h.

2.4. N-TiO_2 treated with H_2O_2 after calcination

The same as above method to prepare nitrogen-doped TiO_2 after calcination at 400 °C for 4 h, then the samples were added to H_2O_2 (40 mL, 7.5 wt.%) and vigorously stirred for 3 h. After washing, the precipitate was dried in oven.

2.5. Characterization

X-ray diffraction (XRD) patterns of all samples were collected in the range 20–80° (2θ) using a Rigaku D/MAX 2550 diffractometer (Cu Kα radiation, λ = 1.5406 Å), operated at 40 kV and 100 mA. The crystallite size was estimated by applying the Scherrer equation to the full width at half-maximum (fwhm) of the (1 0 1) peak of anatase, with α-silicon (99.9999%) as a standard for the instrumental line broadening. The instrument employed for XPS studies was a PerkinElmer PHI 5000C ESCA system with Al Kα radiation operated at 250 W. The shift of the binding energy due to relative surface charging was corrected using the C1s level at 284.6 eV as an internal standard. And the Fourier transform (FT)-IR spectra were recorded with KBr disks containing the powder sample with the FT-IR spectrometer (Nicolet Magna 550). The UV–vis absorbance spectra were obtained for the dry-pressed disk samples using a Scan UV–vis spectrophotometer (Varian, Cary 500) equipped with an integrating sphere assembly, using $BaSO_4$ as the reflectance

sample. The spectra were recorded at room temperature in air within the range 200–800 nm.

2.6. Measurements of photocatalytic activities

The photocatalytic activity was evaluated by measuring the decomposition of the solution of 2,4-dichlorophenol (100 mg/L). A 1000 W halogen lamp was used as the light source of the homemade photo-reactor, surrounded with a water circulation facility at the outer wall through a quartz jacket. The temperature of the photocatalytic reaction was kept below 40 °C. The short wavelength components (λ < 420 nm) of the light were cut off using a glass optical filter. The distance between the lamp and the center of the quartz tube was 10 cm. For a typical photocatalytic experiment, a total of 0.08 g of catalyst powders was added to 80 mL of the above 2,4-dichlorophenol solution in the glass tube. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption/ desorption equilibrium. The above suspensions were kept under constant air-equilibrated conditions before and during the irradiation. At given time intervals, about 4 mL aliquots were sampled, centrifuged, and filtered through a 0.22 μm membrane filter to remove the remaining particles. The filtrates were analyzed by recording variations in the absorption in UV–vis spectra of 2,4-dichlorophenol using a Cary 100 ultraviolet visible spectrometer. According to the standard curve of concentration and absorption, the value of C/C_0 was calculated and indicated the decomposition efficiency.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of the samples are shown in Fig. 1. All samples show the peak at 25.30° which is the main peak (1 0 1) of anatase TiO_2, i.e. different pH values cannot change the crystal structure of TiO_2. Within the detection limits of this technique, all samples present homogeneous catalyst for the anatase crystal structure. The crystal sizes of all the samples are estimated using the Scherrer equation [16]:

$$D = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where B is the half-height width of the diffraction peak of anatase, K = 0.89 is a coefficient, θ is the diffraction angle, and λ is the X-ray wavelength corresponding to the Cu Kα irradiation, and the detailed data are shown in Table 1. The particle sizes vary from 14 to 21 nm. As the pH value increases, the catalyst particle size first increases and then decreases, but the unit cell parameters "d" has
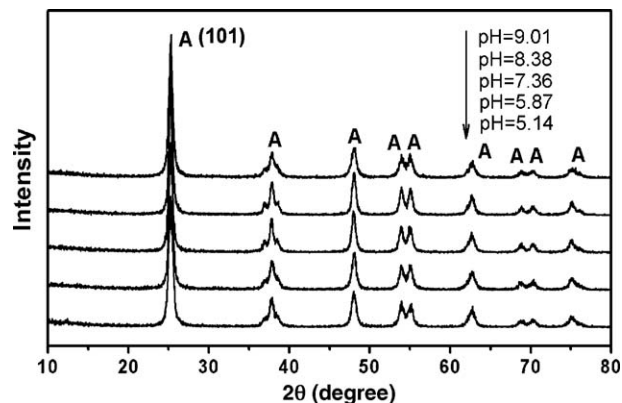

Fig. 1. XRD patterns of N-TiO_2 prepared at different pH values.

Table 1
Some structural characteristics of N-TiO$_2$ at different pH values.

pH	Crystallite size (nm)	d-Spacing (A)
5.14	14.78	3.52
5.87	17.32	3.52
7.36	19.65	3.52
8.38	20.71	3.52
9.01	14.44	3.52

not changed, which implies that the doping process can not change the average unit cell dimension [17]. When pH value was 8.38, the particle has relatively large size and good crystallinity but when the pH value was changed to 5.14 and 9.01, the size of the particle becomes small and the crystallinity is relatively poor. This is the result of the charges on the surface of TiO$_2$ in acidic and alkaline conditions, both of which can restrain the crystallization speed by Coulomb force.

3.2. UV–vis diffuse reflectance spectra

The UV–vis diffuse reflectance spectra of samples prepared at different pH values are presented in Fig. 2. The optical absorption edges of the N-TiO$_2$ are varied with the change of pH values. When the pH value is 8.38, the absorbance region of N-TiO$_2$ is found to be the broadest. Nitrogen doping into the atomic lattice of TiO$_2$ decreases the band gap and thus has a red shift in UV–vis absorption band. Consequently, the optical absorption edges of the doped samples shift to the lower energy region compared to Degussa P-25, and the absorptions after nitrogen doping are drastic and stronger in the range of wavelengths from 400 to 600 nm. The
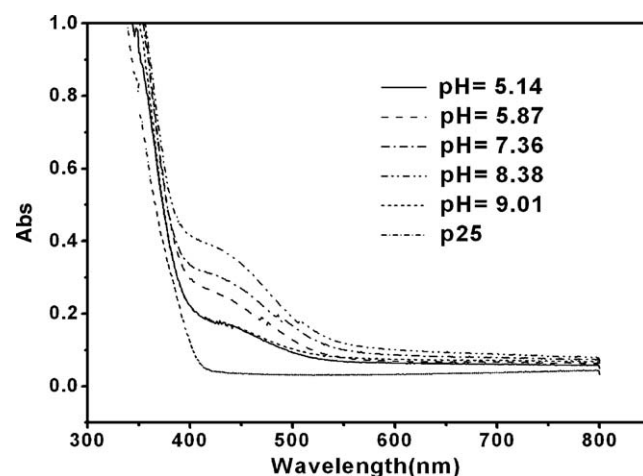
Fig. 2. UV–vis diffuse reflectance spectra of various samples prepared at different pH.

valence band of N-TiO$_2$ consists of N2p and O2p, that is, only donor energy states exist in the band of N-TiO$_2$. As a result, the recombined probability of hole–electron pairs is reduced largely [15].

3.3. XPS spectra

Fig. 3 shows the XPS spectra for the N1s region of N-doped TiO$_2$ at different pH values and its fitting curves. There is a broad peak from 397 to 403 eV. After fitting of the curve, two peaks are obtained at 399 and 401 eV, which are in the range of 396–404 eV
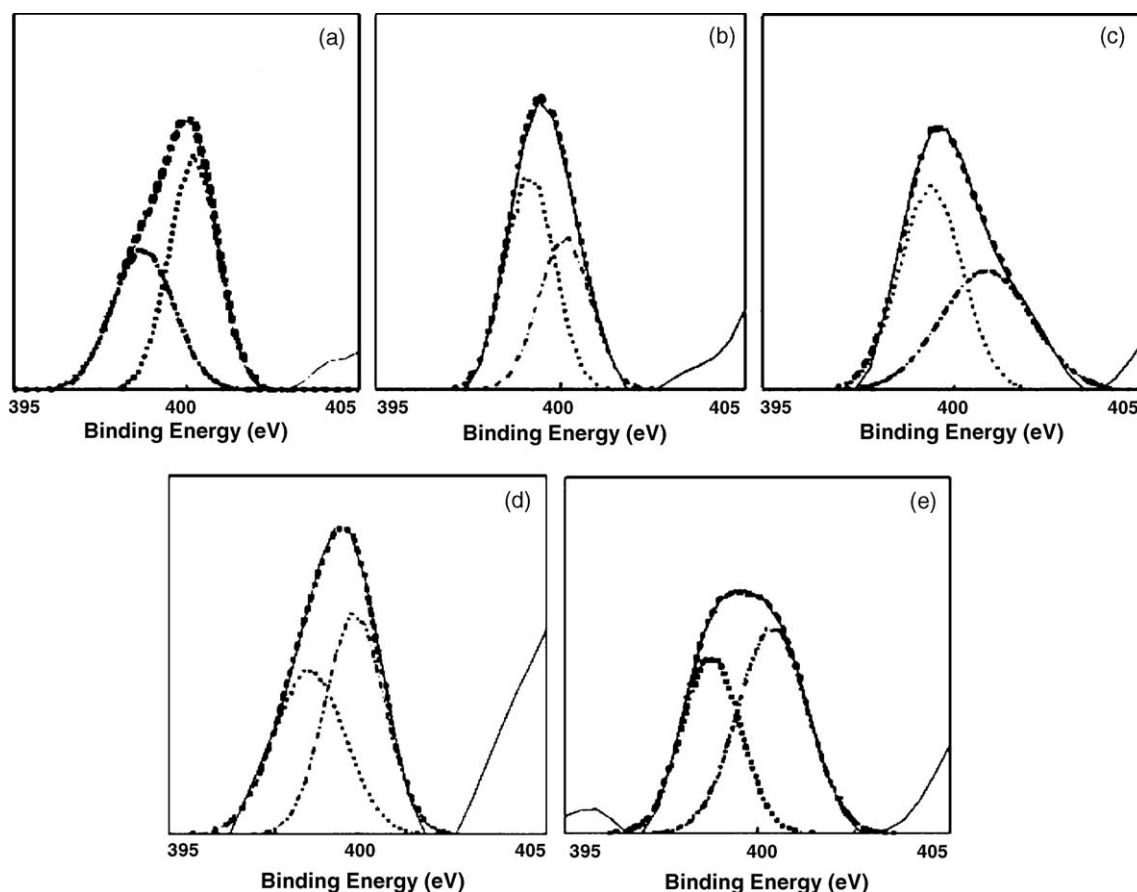
Fig. 3. Fitting XPS spectra for the N1s region of N-doped TiO$_2$ prepared at different pH values: (a) 5.14; (b) 5.87; (c) 7.36; (d) 8.38; (e) 9.01.
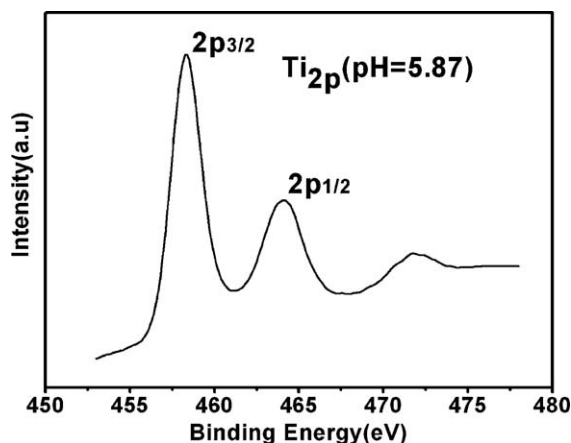
Fig. 4. XPS spectra for the Ti2p region of N-doped TiO_2 at pH value of 5.87.

and considered to be the typical of N-doped TiO_2 by several other researchers [7,18–21]. Generally, the peak in the range of 396–397 eV can be attributed to nitrogen replaces the oxygen in the crystal lattice of TiO_2 due to the binding energy of Ti–N is 397 eV [7]. However, like many other recent published results about N-TiO_2 [7,18,19,21], there is no peak at 396 eV in N1s region of Fig. 3. Instead of that, the peak at 399 eV can be observed, which is attributed to anionic N– in O–Ti–N linkages by many researchers [7,18]. The electro negativity of nitrogen doped into TiO_2 lattice is lower than oxygen, leading to the reducing of electron density on the nitrogen. Therefore, the peak at 399 eV is higher than that of Ti–N appearing at ≤397.5 eV.

The peak at 399 eV could be attributed to nitrogen replaces the oxygen in the crystal lattice of TiO_2. This is also further supported by the results of XPS spectra for the Ti2p region as follows. Fig. 4 shows that the $Ti2p_{3/2}$ and $Ti2p_{1/2}$ core levels of the N-TiO_2 appear at 458.3 and 464.1 eV, respectively. The binding energies of $Ti2p_{3/2}$ and $Ti2p_{1/2}$ after nitrogen doping decrease as compared with pure TiO_2 ($Ti2p_{3/2}$ appears at 459.1 eV and $Ti2p_{1/2}$ appears at 465.0 eV). The different electronic interactions of Ti with N anions cause partial electron transformation from the N to Ti. At the same time, there is an increase of the electron density on Ti due to the lower electro negativity of nitrogen compared with oxygen. This further testifies that nitrogen is incorporated into the lattice and substitutes for oxygen [17,22].

Another peak centered at higher binding energy (401 eV) in XPS spectra for the N1s region is controversial. It is hard to identify this

peak (401 eV) origin from the N1s XPS spectra alone. Therefore, we analyze this peak along with the O1s core levels. As shown in Fig. 5, XPS spectra for the O1s region of N-doped TiO_2, there are two peaks after fitting of the curve. The peak at 529.6 eV is attributed to O1s in Ti–O linkages of TiO_2. Another at 531.4 eV is attributed to the presence of Ti–O–N bonds [23–26]. The peak at about 529.6 and 531.4 eV indicate the presence of two states of oxygen, Ti–O–Ti and Ti–O–N, respectively. Consequently, the presence of Ti–O–N suggests that the peak at 401 eV for N1s region of N-TiO_2 should be attributed to the oxidized nitrogen of Ti–O–N. This oxidized nitrogen of Ti–O–N was chemically adsorbed on the surface of the catalyst and appeared at higher binding energy (401 eV) in the N1s XPS spectra.

From the above observations, it can be concluded that the chemical states of the nitrogen doped in TiO_2 may be various and coexist in the form of N–Ti–O and Ti–O–N. With the increase of calcination temperature in air, part of nitrogen source as NH_4^+ was incorporated into TiO_2 lattice to form N–Ti–O. At the same time part of NH_4^+ was just chemically adsorbed on the surface of photocatalyst and oxidized to form Ti–O–N. Moreover, the nitrogen atom can link with one or more oxygen atoms such as NO^-, NO_2^- or NO_3^- [27].

There are two states of nitrogen doped in the TiO_2. One is doped into the lattice of TiO_2 (N1, 399 eV), another is chemically adsorbed on the surface of the catalyst (N2, 401 eV). The two states of nitrogen doped in TiO_2 are all thought to affect the photocatalytic activity of N-TiO_2 under the visible light by some researchers [28]. It is worth noted that the nitrogen of N2 may restrain the photocatalytic performance, as discussed in Section 3.4.

According to the XPS spectra of the N1s region, different kinds of fitting peak nitrogen percentage in the TiO_2 were calculated in the relation to titanium as shown in Table 2. The XPS is a measurement technique mainly for surface characterization. Moreover, there is error in the calculated nitrogen value in the fitting and calculation process. Table 2 shows that the ratios of N1/Ti and N2/Ti all change obviously under different conditions of preparation. As the pH values increase, the relative contents of two states of nitrogen change a lot, and the highest N1/N2 ratio is shown at pH 5.87 (N1/Ti, N2/Ti and N1/N2 as shown in Table 2). Some researchers have found that the isoelectric point (IEP) of pure TiO_2 is from 5.1 to 6.7 [29–32]. And when the pH is higher than TiO_2 IEP during the preparation of N-TiO_2, the TiO_2 particles demonstrate a strong ability to adsorb NH_4^+, resulting in the increment of N1 and N2. This result is caused by the negative charge of TiO_2 particles at pH 7.36 and above [33]. However, the increment rates of N1 and N2 are different, leading to the
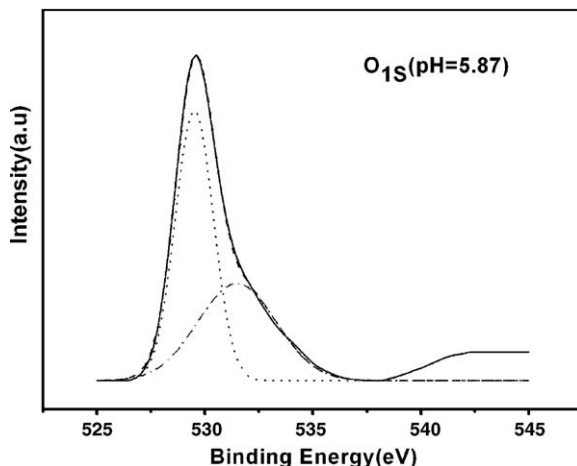

Fig. 5. Fitting XPS spectra for the O1s region of N-doped TiO_2 at pH value of 5.87.

Table 2
Nitrogen doping percentage of N-TiO_2 prepared in different conditions.

	pH 5.14	pH 5.87	pH 7.36	pH 8.38	pH 9.01
N1/Ti	0.00554	0.00479	0.00681	0.00536	0.00700
N2/Ti	0.00591	0.00356	0.00577	0.00598	0.00932
N1/N2	0.938	1.346	1.181	0.896	0.751
		N:Ti = 1		N:Ti = 2		N:Ti = 4
N1/Ti		0.00479		0.00822		0.00397
N2/Ti		0.00356		0.00563		0.00732
N1/N2		1.346		1.460		0.542
		H_2O:Ti = 38		H_2O:Ti = 76		H_2O:Ti = 152
N1/Ti		0.00657		0.00822		0.00348
N2/Ti		0.00429		0.00563		0.00205
N1/N2		1.53		1.460		1.696

N1 is the nitrogen doped into the TiO_2 lattice in the form of N-Ti-O. N2 is the nitrogen chemically adsorbed on the surface of the TiO_2 in the form of Ti-O-N.
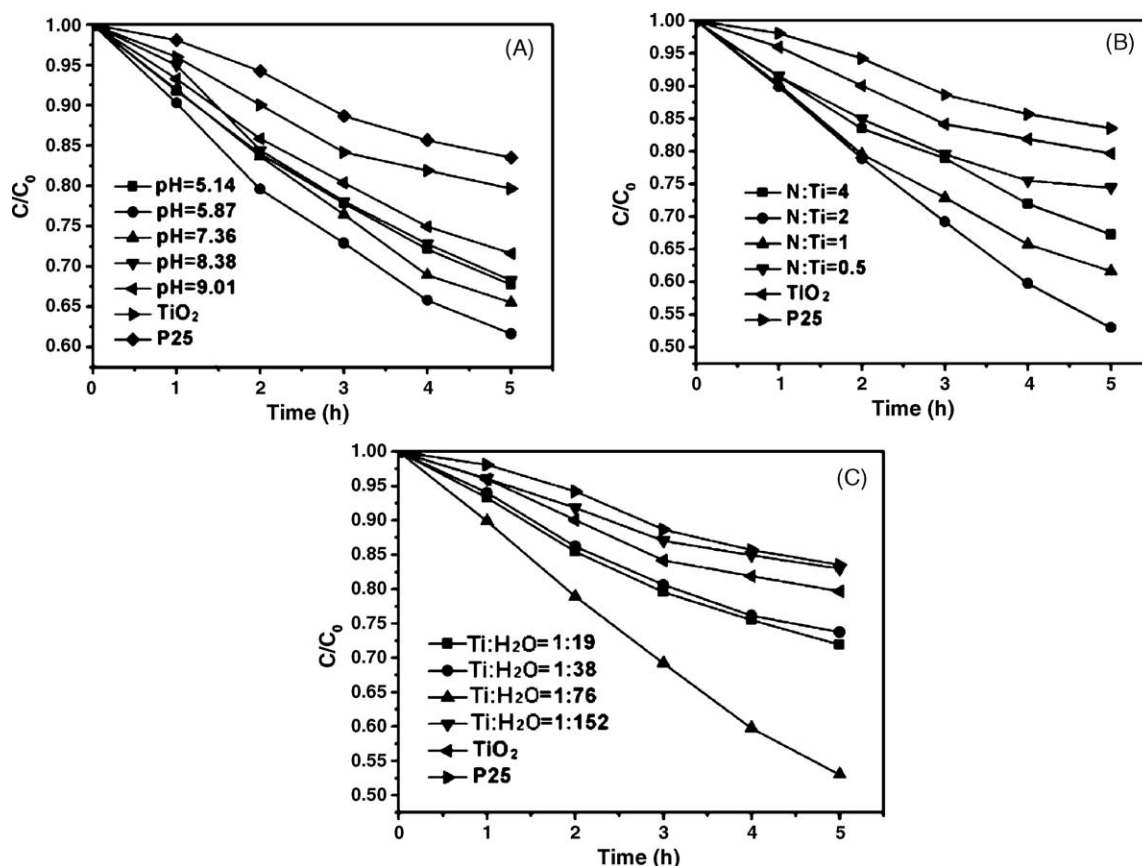
Fig. 6. Photo-degradation rate of 2,4-DCP under visible-light illumination for 5 h on N-TiO$_2$ prepared in different conditions.

difference of N1/N2 (see Table 2). Too high and too low pH value can lead to the protonated TiO$_2$ and the covering of O^{2-} on the surface of TiO$_2$ [34,35], which can further promote the concentration of N2. Therefore, the ratio of N1/N2 is lower at high or low pH value, and there is an optimal ratio of N1/N2 at pH 5.87. In addition, as shown in Table 2 when the N/Ti value increases, the ratio of N1/N2 increases at first and then decreases. However, when the H$_2$O/Ti ratio changes remarkably, the ratio of N1/N2 remains unchanged.

3.4. Evaluation of photocatalytic activity

Fig. 6 shows the photo-degradation rate of 2,4-DCP (100 mg/L) over Degussa P-25, TiO$_2$ and N-TiO$_2$ with different conditions of preparation. Compared to that of undoped TiO$_2$, the photocatalytic activities of N-TiO$_2$ prepared in different conditions are improved greatly and much higher than that of Degussa P-25.

With the increase in pH values, the photocatalytic activity increases at first and then decreases. When the pH value is 5.87, the photo-degradation rate is the highest. Noteworthy, when the pH values increase, the relative contents of two states of nitrogen change a lot (N1/Ti, N2/Ti as shown in Table 2). Generally, the nitrogen of N1 is considered to play a major role in photocatalytic performance of N-TiO$_2$ [17]. However, the photocatalytic activity of N-TiO$_2$ does not increase with the increasing nitrogen of N1 as shown in Fig. 6(A) and Table 2. Interestingly, the catalytic performance of N-TiO$_2$ increases with the increase of N1/N2 ratio. The results suggested that the chemically adsorbed nitrogen of N2 also plays an important role in the photocatalytic performance of N-TiO$_2$.

Burda and coworkers considered that the active sites of the N-doped TiO$_2$ could be passivated by the oxidation states of nitrogen, which led to a less active catalytic surface and less photocatalytic

activity when sintered at high temperature [36]. These oxidation states of nitrogen of N2 cover the surface of catalyst and decrease the number of the active sites. As a result, the photocatalytic activity of N-TiO$_2$ is improved by the doped nitrogen of N1 but reduced by the chemically adsorbed nitrogen of N2. In contrast to this, Joung et al. considered that the active species for N-TiO$_2$ prepared at high temperature may mainly be nitrogen of NO$_2^-$ [28]. Different pH values cause the change of N1 and N2 concentrations, and the photo-degradation rate is affected by these two states of nitrogen.

With the increase of N/Ti ratio (the ratio of NH$_4^+$ to Ti^{4+}), the photo-degradation rate increases at first and then decreases as shown in Fig. 6(B). When the molar ratio of N/Ti is 2, the decomposition rate and the N1/N2 ratio are all the highest which can be obviously observed from Table 2. This further testifies that the nitrogen of N1 could play a key role in the enhancement of visible-light photocatalytic activity. On the other hand, when the N/Ti value is higher than 2, the ratio of N1/Ti and N1/N2 are all decreased. Therefore, we consider that the amount of nitrogen source has an optimal value, which is the N/Ti ratio of 2. Noticeably, when the N/Ti ratios change from 1 to 2, the ratio of N1/N2 changes hardly (from 1.346 to 1.460). However, photocatalytic activity of 2,4-DCP is increased when the N1/Ti ratio is increased from 0.00479 to 0.00822. The results suggest that the nitrogen of N1 could play a major role in the photocatalytic activity of catalyst when the N1/N2 ratio remains unchanged.

In the preparation of photocatalyst, the volume of water is also an important influencing factor. Too much or too less water is harmful to the photocatalytic activity of catalyst. Too much water could accelerate the hydrolytic rate of TBOT, resulting in the increase of the particle size of N-TiO$_2$ but decrease of the photocatalytic activity. Too less water could not make the hydrolysis of TBOT complete,

resulting in the decrease of the photocatalytic activity. Observed from Fig. 6(C), when the H_2O/Ti ratio is 76, the decomposition rate is the highest, but the ratio of N1/N2 is not the highest at this time. Table 2 shows that the H_2O/Ti ratio changes much, but the ratio of N1/N2 changes hardly (about 1.50–1.70). The fact is that when the H_2O/Ti ratio is 76, the N1/Ti ratio is the highest. These results indicate again that the nitrogen of N1 could play a major role in the photocatalytic activity of catalyst when the N1/N2 ratio remains unchanged.

Anyhow, XPS analysis shows the presence of nitrogen species in two states doped in TiO_2. One is doped into the lattice of TiO_2 (N1, 399 eV), another is chemically adsorbed on the surface of catalysts (N2, 401 eV). And the experimental results indicate that these two kinds of N species are all thought to affect the photocatalytic activity of N-TiO_2 under the visible light [28]. The photocatalytic activity of N-TiO_2 is improved by the doped nitrogen of N1. Because the nitrogen replaces the oxygen in the crystal lattice of TiO_2, which results in the reduction of TiO_2 band gap [7]. However, the photo-activity of N-TiO_2 is reduced by the chemically adsorbed nitrogen of N2, due to that the oxidation states of N2 cover the surface of catalysts and decrease the number of active sites [36].

3.5. The influence of H_2O_2 treatment on the preparation of N-TiO_2

The catalysts were treated with hydrogen peroxide, and different kinds of fitting peak nitrogen percentage in the N-TiO_2 were calculated with the relation to the titanium as shown in Table 3. During the preparation of N-TiO_2, NH_4^+ ions as the major nitrogen source were adsorbed on the surface of TiO_2. When the catalyst was treated with H_2O_2 before calcination, the amount of NH_4^+ decreased visibly as shown in Fig. 7. The peak at 1390 cm^{-1} was assigned to the surface adsorbed NH_4^+ [22]. Before calcination, the peak at 1390 cm^{-1} of N-TiO_2 treated with H_2O_2 weakened visibly compared with that of N-TiO_2 without H_2O_2 treatment, which indicated the decrease of NH_4^+ adsorbed on the surface of TiO_2. Because H_2O_2 induced the formation of peroxides adsorbed at TiO_2 surfaces such as Ti–OOH. And the nitrogen species were able to react with peroxides adsorbed at TiO_2 surfaces, producing some
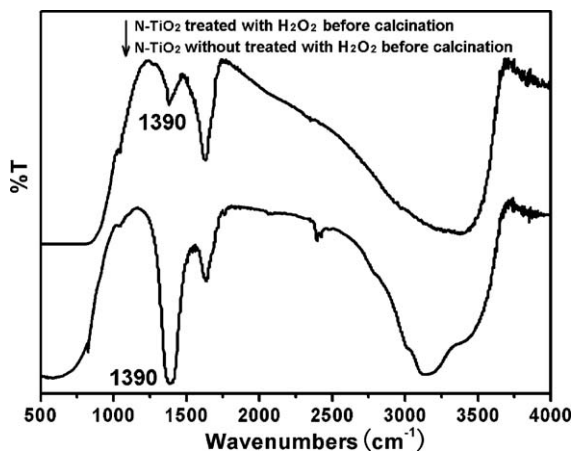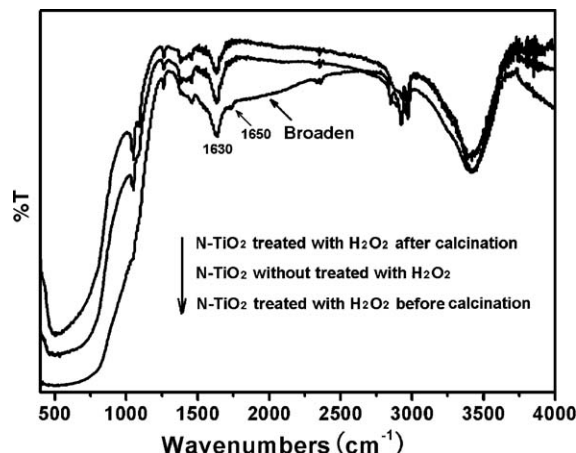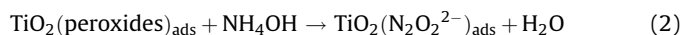

Fig. 8. The FT-IR spectra of different samples after calcination.

nitrogen oxide species that have been identified as hyponitrite species $N_2O_2^{2-}$ [37–40]. The reaction equation was shown as below:

$$TiO_2(peroxides)_{ads} + NH_4OH \rightarrow TiO_2(N_2O_2^{2-})_{ads} + H_2O \qquad (2)$$

The ultraviolet part of solar spectrum could induce the oxidation of hyponitrite species to nitrite and nitrate in the presence of H_2O_2 and O_2 [41–43]. Fig. 8 shows the FT-IR of catalysts treated with H_2O_2 after calcination. After calcination, all the peaks weakened visibly compared with Fig. 7, which indicated the NH_4^+ doping into TiO_2 lattice during high temperature calcination. It is obviously that the FT-IR spectra of N-TiO_2 with H_2O_2 treatment before calcination is different from that of N-TiO_2 without treatment (see Fig. 8). After H_2O_2 treatment, the peak at 1630 cm^{-1} broadened visibly with the range from 1500 to 2000 cm^{-1} which could be attributed to NO_2 stretching vibration [44]. The nitrogen species could be oxidized by O_2 to form NO_2 during high temperature calcination. Furthermore, a new peak at 1650 cm^{-1} appeared after H_2O_2 treatment, which was assigned to the presence of NO_2^- [37]. Therefore, when the catalyst was treated with H_2O_2 before calcination, the NH_4^+ ion was reduced and the oxidation states nitrogen was generated such as NO_2 and NO_2^-. This oxidation states nitrogen could not be doped into TiO_2 lattice, but mostly burnt off by the high temperature sintering. During the calcination process, less nitrogen source of NH_4^+ results into the less concentration of doped nitrogen. Accordingly, the N1/Ti and N2/Ti ratio of N-TiO_2 treated with the H_2O_2 before calcination is much lower than the sample without treated with H_2O_2.

When the catalyst was treated with H_2O_2 after calcination, less NH_4^+ ions were adsorbed on the surface of catalyst. Most of the NH_4^+ ions have been doped into the TiO_2 lattice during the calcination process, which was not oxidized by the hydrogen peroxide. As shown in Fig. 8, the FT-IR spectra of N-TiO_2 treated with H_2O_2 after calcination is changeless compared with that of N-TiO_2 without H_2O_2 treatment. Accordingly, the N1/Ti and N2/Ti ratio of N-TiO_2 treated with the H_2O_2 after calcination remains unchanged compared with that without treated with H_2O_2.

To sum up, the nitrogen was doped into the TiO_2 lattice during the high temperature calcination process. The ammonium ion as a valid nitrogen source can be doped into the TiO_2 lattice while other nitrogen sources such as NO_2 or NO_2^- cannot be doped.

Fig. 9 shows the photo-degradation rate of 2,4-DCP (100 mg/L) over several samples treated with H_2O_2 under visible light. The photocatalytic activity of catalyst treated with H_2O_2 before calcination was the lowest due to a small quantity of nitrogen doped into the TiO_2 lattice and the N1/N2 ratio was also very low.
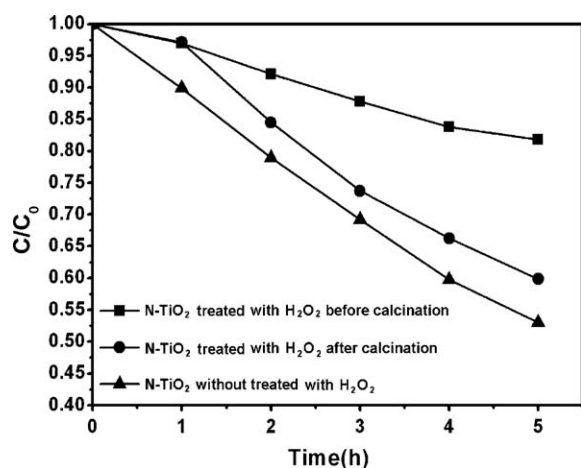

Fig. 7. The FT-IR spectra of different samples before calcination.

Table 3
Nitrogen doping percentage of N-TiO_2 treated with H_2O_2.

	Without treated with H_2O_2	Treated with H_2O_2 before calcinations	Treated with H_2O_2 after calcination
N1/Ti	0.00822	0.00174	0.00730
N2/Ti	0.00563	0.00287	0.00501
N1/N2	1.460	0.606	1.457

Fig. 9. Photo-degradation rate of 2,4-DCP (100 mg/L) under visible-light illumination for 5 h on N-TiO$_2$ treated with H$_2$O$_2$.

The photo-degradation rate shows little difference between the N-TiO$_2$ treated with H$_2$O$_2$ after calcination and the one without treated with H$_2$O$_2$. That is because the N1/N2 and N1/Ti ratio of above two samples are almost unchanged as shown is Table 3. The above experimental results further testified that the two states of doped nitrogen could play a very important role in the photo-catalytic performance N-TiO$_2$.

4. Conclusions

There are two states of nitrogen doped in TiO$_2$. The photocatalytic activity of N-TiO$_2$ is improved by the nitrogen doped into TiO$_2$ lattice. In contrast, the nitrogen chemically adsorbed on the surface of catalyst reduces the photocatalytic performance of N-TiO$_2$. During the preparation of N-TiO$_2$, catalyst was treated with H$_2$O$_2$. We found that only the NH$_4^+$ ion as a valid nitrogen source could be doped into the TiO$_2$ lattice, while other oxidation states nitrogen source such as NO$_2$ or NO$_2^-$ could not.

In addition, ammonia water and ammonium nitrate mixture is used as nitrogen sources to prepare N-TiO$_2$ for the first time, and different pH values can be modified by fixing the total amount of nitrogen sources but changing the NH$_4$NO$_3$/NH$_3$·H$_2$O ratio during the preparation of N-TiO$_2$. The N-TiO$_2$ prepared at pH value of 5.87, N/Ti ratio of 2.0 and H$_2$O/Ti ratio of 76 showed a higher efficiency for photocatalytic degradation of 2,4-dichlorophenol under visible light.

References

[1] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C 1 (2000) 1.
[2] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[3] A.L. Linsebigler, G. Lu, J.T. Yates, J. Chem. Rev. 95 (1995) 735.
[4] H. Kisch, S. Sakthivel, M. Janczarek, D. Mitoraj, J. Phys. Chem. C 111 (2007) 11445.
[5] D.M. Chen, Z.Y. Jiang, J.Q. Geng, Q. Wang, D. Yang, Ind. Eng. Chem. Res. 46 (2007) 2741.
[6] S. In, A. Orlov, R. Berg, F. Garcia, S. Pedrosa-Jimenez, M.S. Tikhov, D.S. Wright, R.M. Lambert, J. Am. Chem. Soc. 129 (2007) 13790.
[7] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269.
[8] T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, M. Matsumura, Appl. Catal. A 265 (2004) 115.
[9] T. Ohno, T. Mitsui, M. Matsumura, Chem. Lett. 32 (2003) 364.
[10] D. Li, H. Haneda, N. Hishita, N. Ohashi, Chem. Mater. 17 (2005) 2588.
[11] T. Umebayashi, T.H. Yamaki, App1. Phys. Lett. 81 (2002) 454.
[12] Y. Cong, J.L. Zhang, F. Chen, M. Anpo, J. Phys. Chem. C 111 (2007) 6976.
[13] B. Chi, L. Zhao, T. Jin, J. Phys. Chem. C 111 (2007) 6189.
[14] S. Livraghi, M.C. Paganini, E. Giamello, A. Selloni, C. Di Valentin, G. Pacchioni, J. Am. Chem. Soc. 128 (2006) 15666.
[15] Z.Q. Liu, Y.P. Wou, Z.H. Li, Y.C. Wang, C.C. Ge, Rare Metals 26 (2007) 263.
[16] J. Lin, Y. Lin, P. Liu, M.J. Meziani, L.F. Allard, Y.P. Sun, J. Am. Chem. Soc. 124 (2002) 11514.
[17] M. Sathishi, B. Viswanathan, R.P. Viswanath, C.S. Gopinath, Chem. Mater. 17 (2005) 6349.
[18] C. Burda, Y. Lou, X. Chen, A.C.S. Samia, J. Stout, J.M. Gole, Nano Lett. 3 (2003) 1049.
[19] S. Sakthivel, M. Janczarek, H. Kisch, J. Phys. Chem. B 108 (2004) 19384.
[20] Y. Cong, L. Xiao, J.L. Zhang, F. Chen, M. Anpo, Res. Chem. Intermed. 32 (2006) 717.
[21] K. Aoki, T. Morikawa, T. Ohwaki, Y. Taga, Chem. Lett. 35 (2006) 616.
[22] H. Li, J. Li, Y. Huo, J. Phys. Chem. B 110 (2006) 1559.
[23] X. Chen, C. Burda, J. Phys. Chem. B 108 (2004) 15446.
[24] J.L. Gole, J.D. Stout, J.C. Burda, Y. Lou, X. Chen, J. Phys. Chem. B 108 (2004) 1230.
[25] E. Gyorgy, P.A. Perezdel, P. Serra, J.L. Morenza, Surf. Coat. Technol. 173 (2003) 265.
[26] N.C. Saha, H.C. Tomkins, J. Appl. Phys. 72 (1992) 3072.
[27] V.C. Di, G. Pacchioni, A. Selloni, S. Livraghi, E. Giamello, J. Phys. Chem. B 109 (2005) 11414.
[28] S.K. Joung, T. Amemiya, M. Murabayashi, K. Itoh, Appl. Catal. A 312 (2006) 20.
[29] G.D. Parfitt, Prog. Surf. Membr. Sci. 11 (1976) 181.
[30] T. Yoko, K. Kamiya, A. Yuasa, K. Tanaka, S. Sakka, J. Non-Cryst. Solids 100 (1998) 483.
[31] A.D. Paola, G. Marci, L. Palmisano, M. Schiavello, K. Uosaki, S. Ikeda, B. Ohtani, J. Phys. Chem. B 106 (2002) 637.
[32] J.J. Sene, W.A. Zeltner, M.A. Anderson, J. Phys. Chem. B 107 (2003) 1597.
[33] X.Z. Li, C.M. Fan, Y.P. Sun, Chemosphere 48 (2002) 453.
[34] Y. Nakaoka, Y. Nosaka, J. Photochem. Photobio1. A 110 (1997) 299.
[35] T. Kasuga, M. Hiramatsu, A. Hoson, Adv. Mater. 11 (1999) 1307.
[36] Y. Zhao, X. Qiu, C. Burda, Chem. Mater. 20 (2008) 2629.
[37] J.A. Navio, C. Cerrillos, C. Real, Surf. Interf. Anal. 24 (1996) 355.
[38] R.I. Bickley, V. Vishwanathan, Nature 280 (1979) 306.
[39] R.I. Bickley, R.K.M. Jayanty, J.A. Navio, C. Real, M. Macias, Surf. Sci. 251/252 (1991) 1052.
[40] J.A. Navio, C. Real, R.I. Bickley, Surf. Interf. Anal. 22 (1994) 417.
[41] Y. Hori, A. Nakatsu, S. Suzuki, Chem. Lett. 14 (1985) 1429.
[42] A. Zafra, J. Garcia, A. Milis, X. Domenech, J. Mol. Catal. 70 (1991) 343.
[43] A. Milis, X. Domenech, J. Photochem. Photobiol. A 72 (1993) 55.
[44] X. Chen, Y. Lou, A.C.S. Samia, C. Burda, J.L. Gole, Adv. Funct. Mater. 15 (2005) 41.